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APPLICANT : NIPPON ZEON CO LTD;

INVENTOR : MAEDA KOICHIRO;

INT.CL. : H01M 4/62

TITLE : BINDER FOR BATTERY, BINDER COMPOSITION, ELECTRODE AND BATTERY

ABSTRACT : PROBLEM TO BE SOLVED: To provide a battery having stable performance by increasing an initial capacity, reducing a capacity decrease and decreasing chipping and crack ing in an electrode surface fixing an active material.

SOLUTION: A polyvinylidene fluoride system polymer (for instance, polyvinylidene fluoride) and a rubber polymer (for instance, polymer obtained as a latex particle by copolymerizing 40 pts.wt. styrene, 30 pts.wt. butadiene, 20 pts.wt. meacrylic acid methyl, 5 pts.wt. acrylonitrile, 5 pts.wt. itaconic acid) are fused or dispersed in a polarity organic solvent (for instance, N-methyl pyrrolidone), a battery binder composition is formed, active material (for instance,  $\text{LiCo}_2$  of positive electrode active material, carbon of negative electrode active material) is compounded therein, obtained slurry is applied to an electrode base unit, the solvent is removed, an electrode is formed, so as to manufacture a battery.

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(54) 【発明の名称】 電池用バインダー、バインダー組成物、電極、および電池

(57) 【要約】

【課題】 初期容量が大きく、容量低下が少なく、さらに活物質を固定した電極表面にひびが入ったり、欠けたりすることと少ないために性能が安定した電池を提供する。

【解決手段】 ポリビニリデンフルオライド系重合体（例えば、ポリビニリデンフルオライド）とゴム質重合体（例えば、スチレン40重量部、ブタジエン30重量部、メアクリル酸メチル20重量部、アクリロニトリル5重量部、イタコン酸5重量部を共重合してラテックス粒子として得られたポリマー）を極性有機溶媒（例えば、N-メチルピロリドン）溶解、または分散させてなる電池用バインダー組成物に活物質（例えば、負極活物質である炭素、正極活物質であるLiCoO<sub>2</sub>）を配合したスラリーを電極基体に塗布、溶媒除去して電極とし、電池を製造する。

## 【特許請求の範囲】

【請求項1】 ポリビニリデンフルオライド系重合体とゴム質重合体からなる電池用バインダー。

【請求項2】 ゴム質重合体が極性ゴム質重合体である請求項1記載の電池用バインダー。

【請求項3】 ゴム質重合体が芳香族ビニル・共役ジエン系共重合体である請求項1または2記載の電池用バインダー。

【請求項4】 請求項1、2、または3記載の電池用バインダーと溶媒からなるバインダー。

【請求項5】 請求項1、2、または3記載の電池用バインダーによって活物質を固定した電極。

【請求項6】 請求項5記載の電極を用いた電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は電池用バインダー組成物、それを用いた電極、および電池に関し、さらに詳しくは、電池の容量が大きく、充放電を繰り返しても劣化の少ない電池用バインダー組成物、それを用いた電極、および電池に関する。

## 【0002】

【従来の技術】電池用バインダーは、電極基体表面上と接着し、バインダー構造中に活物質が固定された状態にすることにより、電極表面に活物質を固定する。電池の容量は、活物質の種類、量、電解液の種類、量などの複数の要因によって決められるが、バインダーが充分量の活物質を電極に固定できないと初期容量の大きな電池が得られず、また、充放電を繰り返すことなどによって電極から活物質が脱落するに従って電池の容量は低下する。

【0003】電池用バインダーは、通常、バインダーとなる重合体を溶媒に溶解または分散したバインダー組成物に活物質を分散させて、電極基体表面に塗布し、溶媒を揮発させることにより、電極表面に活物質を固定する。

【0004】バインダー組成物には、有機溶媒系バインダー組成物と水系バインダー組成物の二種類があり、有機溶媒系バインダー組成物としては、通常、ポリビニリデンフルオライドなどのポリビニリデンフルオライド系重合体をN-メチルピロリドンなどの有機溶媒に溶解したものが用いられている（例えば、特開平4-249860号公報、特開平7-201315号公報、特開平7-201316号公報など）。この有機溶媒系バインダー組成物に活物質を分散させたスラリーを電極基体に塗布して、有機溶媒を除去して製造した電極を用いると電池の初期容量を大きくすることができるが、この電極を用いた電池で充放電を繰り返すと電極に固定された活物質が脱落しやすいという問題がある。極性基を有するコモノマーを共重合することにより極性を導入することにより活物質が電極基体から脱落しにくいように改良した場

合（例えば、特開平7-201315号公報、特開平7-201316号公報など）においても、ポリビニリデンフルオライド系重合体からなるバインダーでは改良効果が小さく、また、電解液に膨潤して強度が低下しやすくなるためなどにより、脱落を十分に抑制できなかった。

【0005】水系バインダー組成物としては、界面活性剤を用いた乳化重合法により水を溶媒として製造されたスチレン・ブタジエン共重合ゴムのラテックスの水分散液に、増粘剤としてカルボキシルメチルセルロースなどを添加したものが用いられている（例えば、特開平4-342966号公報、特開平5-21068号公報、特開平5-74461号公報など）。この水系バインダー組成物に活物質を分散させたスラリーを電極基体に塗布して、水分を除去して製造した電極を用いると、活物質が脱落しにくくなるため、充放電を繰り返しても電極から活物質が脱落しにくいのが、容量の大きな電池は得られなかった。

## 【0006】

【発明が解決しようとする課題】本発明の目的は、電池の容量を大きくでき、充放電を繰り返しても劣化の少ない電池用バインダー組成物、それを用いて活物質を固定した電極、および電池を提供することにある。

## 【0007】

【課題を解決するための手段】本発明者らは、鋭意努力の結果、ポリビニリデンフルオライド系重合体にゴム質重合体を配合した組成物がバインダーとして活物質を脱落させにくいことを見出し、本発明を完成させるに至った。

【0008】かくして、本発明によれば、ポリビニリデンフルオライド系重合体とゴム質重合体からなる電池用バインダー、該電池用バインダーと溶媒からなるバインダー、該電池用バインダーによって活物質を固定した電極、および該電極を用いた電池が提供される。

## 【0009】

## 【発明の実施の形態】

（ポリビニリデンフルオライド系重合体）本発明で用いるポリビニリデンフルオライド系重合体は、ビニリデンフルオライドに由来する繰り返し構造単位を50重量%以上、好ましくは80重量%以上、より好ましくは90重量%以上、通常の場合は100重量%が最も好ましい。ビニリデンフルオライドに由来する繰り返し構造単位が少なすぎると、柔軟性が不足するか、耐溶剤性が低く、活物質を十分に固定し、脱落させずに維持させることが困難になる。

【0010】必要に応じて、活物質を十分に固定し、脱落させずに保持できる範囲で、ビニリデンフルオライドと共重合可能なコモノマーを用いて共重合体としてもよい。そのようなコモノマーとしては、エチレン性不飽和単体が挙げられ、例えば、スチレン、 $\alpha$ -メチルスチ

レン、ビニルトルエン、p-tert-ブチルスチレン、クロロスチレンなどの芳香族ビニル系単量体；（メタ）アクリル酸メチル、（メタ）アクリル酸エチル、（メタ）アクリル酸プロピル、（メタ）アクリル酸ブチル、（メタ）アクリル酸イソブチル、（メタ）アクリル酸2-エチルヘキシルなどの（メタ）アクリル酸エステル系単量体；（メタ）アクリルアミド、N-メチロール（メタ）アクリルアミド、N-ブトキシメチル（メタ）アクリルアミドなどの（メタ）アクリルアミド系単量体；（メタ）アクリル酸グリシジル、アリルグリシジリエーテルなどのグリシジル基含有単量体；（メタ）アクリロニトリルなどの（メタ）アクリロニトリル系単量体；

アクリル酸、メタクリル酸、クロトン酸、フマル酸、イタコン酸などのカルボキシル基含有単量体；スチレンスルホン酸ソーダ、アクリルアミドメチルプロパンスルホン酸などのスルホン酸基含有単量体；メタクリルジメチルアミノエチル、メタクリル酸ジエチルアミノエチルなどのアミノ基含有単量体；などが挙げられる。

これらの大半は極性基を有する単量体であるが、バインダーが接着性に優れたものにするために、ポリビニリデンフルオライド系重合体を共重合体とする場合のコモノマーとしては、極性基を有する単量体を用いるのが好ましい。その場合、コモノマーに由来する繰返し構造単位が5重量%以下、好ましくは20重量%以下、より好ましくは10重量%以下になるように共重合する。コモノマー由来の繰返し構造単位が多すぎると、ビニリデンフルオライド由来繰返し構造単位が少なくなりすぎ、耐溶剤性が低く、充放電による体積変化によって活物質が電極基体から脱落しやすくなるという問題を生じる。

【0011】本発明のポリビニリデンフルオライド系重合体は、水性溶媒や有機溶媒中で、過硫酸塩、過リン酸塩などを重合開始剤として用いて、重合温度40～140℃、重合圧力1.4～14MPa、重合開始剤、乳化剤、連鎖移動剤を用いて共重合して得ることができる。なお、重合度が好ましくは500以上、より好ましくは800以上、かつ好ましくは3000以下、より好ましくは2000以下にする。重合度が小さすぎるとバインダーとして強度が不足し、大きすぎると粘度が高くなりすぎ、バインダー組成物を塗布するのが困難になる。

【0012】（ゴム質重合体）本発明においては、バインダーをより柔軟性に優れたものにするために、ポリビニリデンフルオライド系重合体にゴム質重合体を配合してバインダーとする。ゴム質重合体は、特に限定されないが、バインダーとして、活物質との密着性に優れ、電極基体と活物質の接着に優れる点で極性を有するゴム質重合体が好ましい。

【0013】極性ゴム質重合体は、極性を有する単量体（以下、極性単量体という）に由来する繰返し構造単位を好ましくは5重量%以上、より好ましくは10重量

%以上、特に好ましくは30重量%以上、100重量%以下含有するゴム質重合体である。極性単量体由来繰返し構造単位が少ないと極性が小さく、活物質が電極基体から剥離しやすいという問題を生じる場合があり、また、有機溶媒に分散しにくくなる。極性単量体としては、（メタ）アクリロニトリル、クロトンニトリル、アリルニトリルなどのエチレン性ニトリル化合物；メチル（メタ）アクリレート、エチル（メタ）アクリレート、ブチル（メタ）アクリレート、（メタ）アクリロニトリル、ヒドロキシエチル（メタ）アクリレートなどのエチレン性不飽和カルボン酸エステル；アクリル酸、メタクリル酸、イタコン酸、フマル酸、マレイン酸などのエチレン性不飽和カルボン酸；無水マレイン酸などのエチレン性不飽和カルボン酸無水物；などを使用することができる。特に、イタコン酸、フマル酸、マレイン酸などのジカルボン酸や無水マレイン酸などのジカルボン酸無水物などが電極の接着強度を高める点で好ましい。

【0014】また、強度と柔軟性のバランスがよいことから、極性ゴム質重合体は、芳香族ビニル・共役ジエン系重合体であることが好ましい。この好ましい芳香族ビニル・共役ジエン系重合体は、上記の極性単量体に由来する繰返し構造単位が5重量%以上、好ましくは10重量%以上、より好ましくは30重量%以上、かつ好ましくは50重量%以下、より好ましくは40重量%以下、特に好ましくは35重量%以下、スチレン、 $\alpha$ -メチルスチレン、ビニルトルエン、p-tert-ブチルスチレンなどの芳香族ビニル系単量体に由来する繰返し構造単位が好ましくは15重量%以上、より好ましくは20重量%以上、特に好ましくは25重量%以上、かつ好ましくは50重量%以下、より好ましくは45重量%以下、特に好ましくは40重量%以下、1、3-ブタジエン、イソプレン、2、3-ジメチル-1、3-ブタジエン、1、3-ペンタジエンなどの共役ジエン系単量体に由来する繰返し構造単位が好ましくは15重量%以上、より好ましくは20重量%以上、特に好ましくは30重量%以上、かつ好ましくは80重量%以下、より好ましくは50重量%以下、特に好ましくは40重量%以下である。極性単量体が多すぎると芳香族ビニル・共役ジエン系重合体の特性があらわれにくく、柔軟性に劣る。芳香族ビニル系単量体が多すぎると共役ジエン系単量体が多すぎると強度が不足し、芳香族ビニル系単量体が多すぎると共役ジエン系単量体が多すぎると柔軟性が不足する。強度が不足すると充放電による活物質の膨潤・収縮という体積変化のために活物質が電極基体から脱落しやすく、柔軟性が不足すると電極が歪むために電池を組み立てる際に電極のわずかな変形によってもバインダーが電極基体から剥離しやすくなり、活物質が電極基体から脱落しやすい。

【0015】本発明に用いるゴム質重合体の製造方法は

特に限定されず、極性ゴム質重合体である芳香族ビニル・共役ジエン系重合体の場合も、溶液重合でも乳化重合でもよいが、通常、簡便であることなどから、乳化重合によりラテックス粒子として重合される。乳化重合をする場合、一般には、単量体混合物100重量部を水を主成分とする分散媒60重量部以上、好ましくは100重量部以上、かつ300重量部以下、好ましくは200重量部に分散させ、乳化剤1重量部以上、好ましくは2重量部以上、かつ10重量部以下、好ましくは7重量部以下、重合開始剤0.1重量部以上、好ましくは0.2重量部以上、かつ1重量部以下、好ましくは0.6重量部以下、さらに必要量の分子量調節剤を加えて、温度30℃以上、好ましくは50℃以上、かつ100℃以下、好ましくは90℃以下で攪拌しながら重合する。単量体全部を予め分散媒に分散させた後に重合するバッチ方式、単量体の一部を重合させた後に残りの単量体を連続的に分散媒に添加して重合するセミバッチ方式、単量体を連続的に分散媒に添加して重合する連続方式のいずれで重合してもよい。乳化剤としては、ポリオキシエチレンアルキルエーテル類、ポリオキシエチレンアルキルフェノールエーテル類、ポリオキシエチレンオキシド・ポリプロピレンオキシド共重合体などの非イオン性乳化剤；アルキルスルホネート類、アルキルアシルスルホネート類、アルキルスルフェート類、アルキルスルホサクシネート類、ポリオキシエチレンアルキルフェニルエーテルサルケート類などのアニオン性乳化剤が挙げられる。重合開始剤としては、過硫酸カリウム、過硫酸アンモニウムなどの過硫酸塩；過酸化水素、ベンゾイルパーオキシド、クメンパーオキシド、第三ブチルヒドロパーオキシドなどの過酸化物質；などを用い、必要に応じて重亜硫酸ソーダ、アスコルビン酸などの還元剤；燐酸二ナトリウムなどの重合助剤を併用してもよい。

【0016】なお、乳化重合で極性ゴム質重合体である芳香族ビニル・共役ジエン系重合体を得た場合、ラテックス粒子として得られたポリマーの粒子径は0.01 $\mu$ m以上、好ましくは0.05 $\mu$ m以上、より好ましくは0.10 $\mu$ m以上、かつ10 $\mu$ m以下、好ましくは1 $\mu$ m以下、より好ましくは0.5 $\mu$ m以下である。また、溶液重合で極性ゴム質重合体である芳香族ビニル・共役ジエン系重合体を得た場合、テトラヒドロフランを溶媒とするゲル・パーミエーション・クロマトグラフィによるポリスチレン換算値で重量平均分子量20,000以上、好ましくは30,000以上、より好ましくは50,000以上、かつ1,000,000以下、好ましくは800,000以下、より好ましくは500,000以下である。粒径や分子量が小さすぎると接着性に劣り、電極基体から活物質が脱落しやすくなり、大きすぎると重合が困難である。

【0017】（電池用バインダー）本発明の電池用バインダーは、ポリビニリデンフルオライド系重合体100

重量部に対して、ゴム質重合体5重量部以上、好ましくは20重量部以上、より好ましくは40重量部以上、かつ100重量部以下、好ましくは90重量部以下、より好ましくは80重量部以下配合したものである。ゴム質重合体が少なすぎると柔軟性がないため、わずかな電極の歪みなどでバインダーが電極基体から剥離しやすく、電極表面の活物質層が割れたり、欠けたりすることがある。逆に多すぎると強度が不足し、充放電による活物質の体積変化により活物質が脱落しやすくなる。

【0018】（電池用バインダー組成物）本発明の電池用バインダー組成物は、電池用バインダーの溶液または分散液であるが、通常は簡便であることから、予めバインダーを調製することなく、ポリビニリデンフルオライド系重合体、ゴム質重合体、その他の任意成分を一つの溶媒に溶解または分散させてバインダー組成物を調製する。

【0019】溶媒は、ポリビニリデンフルオライド系重合体とゴム質重合体を溶解、または分散できるものであれば、特に限定されない。特に、ゴム質重合体を極性ゴム質重合体にするにより、ポリビニリデンフルオライド系重合体がよく溶解、または分散できるN-メチルピロリドン、ジメチルフルオライドなどの極性有機溶媒に、ゴム質重合体も分散させることができる。なお、通常、ポリビニリデンフルオライドが溶解しないアセトン、メチルエチルケトン、メチルイソブチルケトンなどのケトン類；テトラヒドロフラン、ルルフラールなどのフラン類；酢酸エチル、酢酸メチルなどのエステル類；アセトニトリル、プロピオニトリルなどのニトリル類；などについても、ポリビニリデンフルオライド系重合体で使用したコモノマーの種類、量によっては可溶となり、これらの溶媒も、ゴム質重合体が溶解、分散できる限りは使用できる。

【0020】溶媒量も特に限定されないが、通常、バインダー100重量部に溶媒を好ましくは400重量部以上、より好ましくは500重量部以上、特に好ましくは800重量部以上、かつ好ましくは10,000重量部以下、より好ましくは5,000重量部以下、特に好ましくは2,000重量部以下にする、多すぎても少なすぎてもバインダー組成物を塗布するのが困難になる。

【0021】（電極）本発明の電極は、電池用バインダー組成物に活物質を配合してスラリーを調製し、電極基体に塗布し、溶媒を除去することにより、電極基体表面に形成されたバインダーのマトリックス中に活物質を固定することにより得られる。

【0022】本発明で用いる活物質は、活物質として機能する限り特に限定されず、通常は、負極活物質として炭素を用い、正極活物質としてモリブデン、バナジウム、チタン、ニオブなどの酸化物、硫化物、セリン化物などのほか、リチウムマンガニ酸化物、リチウムコバルト酸化物、リチウムニッケル酸化物、リチウム鉄酸化物



などのリチウム含有複合酸化物などが用いられる。固定する活物質としては、バインダーマトリックス中に特にしっかりと固定され、電池の電極としての使用中に脱落しにくいことから、炭素が好ましい。

【0023】本発明に用いるスラリーの活物質質量も特に限定されないが、電池用バインダーに対して、重量基準で好ましくは5倍以上、より好ましくは7倍以上、かつ1000倍以下、より好ましくは100倍以下になるよう電池用バインダー組成物に活物質を配合したものである。活物質質量が少なすぎると活物質を固定したバインダー層表面に不活性な部分が多くなり、電極としての機能が不十分となることがあり、活物質が多すぎると活物質が電極基体に十分に固定されずに脱落しやすくなる。なお、スラリーは、溶媒を追加して、塗布しやすい濃度にして使用する。

【0024】本発明に用いる電極基体は導電性材料からなるものであれば特に限定されないが、一般には鉄、銅、アルミニウムなどの金属製のものを用いる。形状も特に限定されないが、電極表面積が大きいものが好ましいことから、通常、厚さ0.05~0.5mm程度のシートを用いる。

【0025】スラリーを塗布する方法は特に限定されない。例えば、浸漬、ハケ塗りなどによって塗布される。塗布する量は、有機溶媒を除去した後に形成される活物質を固定したバインダー層の厚さが好ましくは0.1mm以上、より好ましくは0.5mm以上、好ましくは5mm以下、より好ましくは2mm以下になるようにする。有機溶媒を除去する方法も特に限定されないが、通常は、応力集中が起こってバインダー層に亀裂がはいったり、電極基体から剥離したりしない程度の速度範囲で、できるだけ早く有機溶媒が揮発するように、減圧の程度、加熱の程度を調整して有機溶媒を除去する。

【0026】(電池)本発明の電池は、正極と負極の少なくとも一方に本発明の電極を用いたものである。この電池は、正極と負極を活物質が固定されている側(本発明の電極においては、バインダー層側)を向かい合わせ、両極の間に電解液を満たした構造を有している。大型の電池の場合には、電極をテープ状のものとし、負極と正極の間にセパレーター・シートを挟みこんで巻回し、電解液を満たしたケース中に浸漬するなどの方法で、また小型電池の場合には、電極を円状のシートにして電解液を満たしたコイン型ケース中に浸漬するなどの方法で電池として使用しやすく、かつ大きな容量のものが得られるようにすることができる。

【0027】電解液も特に限定されず、負極活物質、正極活物質の種類に応じて、電池としての機能を発揮するものを選択すればよい。例えば、電解質として、 $\text{LiClO}_4$ 、 $\text{LiBF}_4$ 、 $\text{CF}_3\text{SO}_3\text{Li}$ 、 $\text{LiI}$ 、 $\text{LiAlCl}_4$ 、 $\text{LiPF}_6$ 、 $\text{NaClO}_4$ 、 $\text{NaBF}_4$ 、 $\text{NaI}$ 、 $(n\text{-Bu})_4\text{NClO}_4$ などが例示され、溶媒として、

エーテル類、ケトン類、ラクトン類、ニトリル類、アミン類、アミド類、硫黄化合物類、塩素化炭化水素類、エステル類、カーボネート類、ニトロ化合物類、リン酸エステル系化合物類、スルホラン系化合物類などが例示され、一般には、エチレンカーボネートやジエチルカーボネートなどが広く使用されている。

【0028】(態様)本発明の態様としては、(1) ポリビニリデンフルオライド系重合体とゴム質重合体からなる電池用バインダー、(2) ゴム質重合体が極性ゴム質重合体である(1)記載の電池用バインダー、

(3) ゴム質重合体が極性基を有する単量体由来する繰返し構造単位を5~100重量%含有するものである(1)または(2)記載の電池用バインダー、

(4) ゴム質重合体が芳香族ビニル・共役ジエン系共重合体である(1)~(3)のいずれかに記載の電池用バインダー、

(5) ゴム質重合体が、極性基を有する単量体由来する繰返し構造単位が5~50重量%、芳香族ビニル系単量体由来する繰返し構造単位が15~50重量%、共役ジエン系単量体由来する繰返し構造単位が15~80重量%含有するものである(1)~(4)のいずれかに記載の電池用バインダー、

(6) ゴム質重合体が粒径0.01~1.0 $\mu\text{m}$ のラテックス粒子である(1)~(5)のいずれかに記載の電池用バインダー、

(7) ゴム質重合体がテトラヒドロフランを溶媒とするゲル・パーミエーション・クロマトグラフィによるポリスチレン換算値で重量平均分子量20,000~1,000,000である(1)~

(5)のいずれかに記載の電池用バインダー、(8) ポリビニリデンフルオライド系重合体がビニリデンフルオライド由来する繰返し構造単位を50~100重量%含有している(1)~(7)のいずれかに記載の電池用バインダー、(9) ポリビニリデンフルオライド系重合体の重合度が500~3,000である(1)~(8)のいずれかに記載の電池用バインダー、(10)

ポリビニリデンフルオライド系重合体100重量部に対して、ゴム質重合体5~100重量部配合したものである(1)~(9)のいずれかに記載の電池用バインダー、(11) 溶媒と(1)~(10)のいずれかに記載の電池用バインダーからなる電池用バインダー組成物、(12) 電池用バインダー100重量部に溶媒を400~10,000重量部加えたものである(11)記載の電池用バインダー組成物、(13) (1)~(10)のいずれかに記載の電池用バインダーによって活物質を固定した電極、(14) 電池用バインダーに対して、重量基準で好ましくは5~1000倍の活物質を固定した(13)記載の電極、(15) (1)~(10)のいずれかに記載の電池用バインダー組成物に活物質を均一分散させ、電極基体に塗布し、溶媒を除去した電極、(16) (13)~(15)のいずれかに記載の電極を正極、負極の少なくとも一方に用いた電

池、などが例示される。

#### 【0029】

【実施例】以下に、参考例、実施例、比較例を挙げて、本発明を具体的に説明する。

#### 【0030】参考例1

水1リットルにスチレン400g、ブタジエン300g、メタクリル酸メチル200g、アクリロニトリル50g、イタコン酸50g、ラウリル硫酸アンモニウム4g、重炭酸ナトリウム10gを加えて攪拌し、モノマーエマルジョンを調製した。

【0031】水3.4リットル、エチレンジアミン四酢酸10g、ラウリル硫酸アンモニウム10g、過硫酸カリウム20gと上記モノマーエマルジョンの10重量%を加え、攪拌しながら80℃に加熱して、1時間反応させ、過硫酸カリウム80gを水200mlとともに加えた後、残りのモノマーを4時間に渡って連続的に等速度で添加し、さらに4時間反応させた。残留していたモノマーを減圧して除去し、水酸化リチウムでpHを7に調整した。なお、転化率は約99%であった。

【0032】得られたラテックス分散液250mlに2000gのN-メチルピロリドンを加え、エバポレーターを用いて水分を除去してラテックス粒子有機溶媒分散液を得た。このラテックス粒子有機溶媒分散液は固形分濃度9.3重量%、水分約180ppm、ラテックス粒子の平均粒子径は0.18μmであった。

#### 【0033】参考例2

スチレン400g、ブタジエン300g、メタクリル酸メチル200g、アクリロニトリル50g、イタコン酸50gの代わりに、スチレン500g、ブタジエン250g、メタクリル酸メチル150g、アクリロニトリル100gを用いる以外は実施例1と同様にしてラテックス粒子有機溶媒分散液を得た。このラテックス粒子有機溶媒分散液は固形分濃度7.0重量%、水分約200ppm、ラテックス粒子の平均粒子径は0.18μmであった。

#### 【0034】参考例3

スチレン400g、ブタジエン300g、メタクリル酸メチル200g、アクリロニトリル50g、イタコン酸50gの代わりに、スチレン350g、ブタジエン200g、メタクリル酸メチル200g、アクリロニトリル100g、イタコン酸100g、フマル酸50gを用いる以外は実施例1と同様にしてラテックス粒子有機溶媒分散液を得た。このラテックス粒子有機溶媒分散液は固形分濃度4.0重量%、水分180ppm、ラテックス粒子の平均粒子径は0.18μmであった。

#### 【0035】実施例1

N-メチルピロリドン30重量部にポリビニリデンフルオライド（重合度約1000）5重量部と参考例1で得たラテックス粒子有機溶媒分散液を固形分量が3重量部になるように加えて、本発明のバインダー組成物を得

た。

【0036】このバインダー組成物に組成物中の固形分量8重量部に対して負極活物質であるカーボン（関西熱学製、NG-12L）100重量部を加え、粘度が約7000cpsになるようにN-メチルピロリドンを加えて、スラリーを調製し、厚さ0.1mmの銅箔上に塗布し、130℃に5時間保持して乾燥し、ロールプレスにより厚さが0.5mm均一の活物質を固定したバインダー層を形成して本発明の電極（負極）とした。

【0037】また、同じバインダー組成物に組成物中の固形分量4重量部に対して、正極活物質であるLiCoO<sub>2</sub>90重量部とアセチレンブラック（電気化学工業製、デンカブラック）10重量部を加え、粘度が約7000cpsになるようにN-メチルピロリドンを加えて、スラリーを調製し、厚さ0.05mmのアルミ箔上に塗布し、130℃に5時間保持して乾燥し、ロールプレスにより厚さが0.5mm均一の活物質を固定したバインダー層を形成して電極（正極）を製造した。

【0038】負極と正極の両電極をテフロン板上で、筒状の刃を用いて直径15mmの円形に切り抜いた。バインダーによって固定化された活物質層の切断部で、ひび割れや欠けなどは認められなかった。

【0039】この両電極を直径16mm、厚さ50μmの円形のポリプロピレン製微多孔膜（繊維不織布）からなるセパレーターを介在させて、互いにバインダーで固定化した活物質層を対向させて、ポリプロピレン製バックギンを配置したステンレス鋼製の外装容器中（直径20mm、高さ1.8mm、ステンレス鋼厚さ0.2mmの底面が一つだけある円筒状容器）に収納した。容器中に、エチレンカーボネートとジエチルカーボネートを容積比で1:1に混合した溶媒にLiPF<sub>6</sub>を1mol/lの濃度に溶解した電解液を空気が残らないように注入して、厚さ0.2mmのステンレス鋼のキャップをかぶせて、ポリプロピレン製バックギンを介して外装容器とキャップを固定し、それぞれキャップに銅箔が、容器底面にアルミ箔が接触するように内容物を封止して、直径20mm、厚さ2.0mmのコイン型電池を製造した。

【0040】この電池に、定電流法（電流密度：1.0mA/cm<sup>2</sup>）で4.0Vに充電し、3.0Vまで放電する充放電を行い、容量の変化を測定した。1回目の充電での容量は180mAh（100%）であり、50回目の充電では170mAh（約94%に低下）、100回目の充電では160mAh（約89%に低下）であった。

#### 【0041】実施例2

参考例1で得たラテックス粒子有機溶媒分散液の代わりに参考例2で得たラテックス粒子有機溶媒分散液を用いる以外は、実施例1と同様に電極を作製し、電池を得、性能を調べた。

【0042】直径15mmの円形に切り抜いた両電極のバインダーによって固定化された活物質層の切断部で、ひび割れや欠けなどは認められなかった。また、1回目の充電での容量は175mAh(100%)であり、50回目の充電では160mAh(約91%に低下)、100回目の充電では155mAh(約89%に低下)であった。

【0043】実施例3

参考例1で得たラテックス粒子有機溶媒分散液の代わりに参考例3で得たラテックス粒子有機溶媒分散液を用いる以外は、実施例1と同様に電極を作製し、電池を得、性能を調べた。

【0044】直径15mmの円形に切り抜いた両電極のバインダーによって固定化された活物質層の切断部で、ひび割れや欠けなどは認められなかった。また、1回目の充電での容量は185mAh(100%)であり、50回目の充電では170mAh(約92%に低下)、100回目の充電では160mAh(約86%に低下)であった。

【0045】比較例1

調製したバインダー組成物の代わりにN-メチルピロリドン90重量部にポリビニリデンフルオライド10重量部を加えたバインダー組成物を用いる以外は実施例1と同様にして電極を作製し、電池を得、性能を調べた。

【0046】直径15mmの円形に切り抜いた両電極のバインダーによって固定化された活物質層の切断部で、ひび割れが認められ、またかなりの部分で欠けが認められた。また、1回目の充電での容量は180mAhであったが、40回目で20mAh以下まで低下したので測定を中止した。

【0047】

【発明の効果】本発明の電池用バインダー組成物を用いて活物質を固定した電極を正極・負極のいずれか一方に用いた電池においては、その電極から活物質が脱落しにくいため容量低下が小さく、初期容量が大きく、さらに活物質を固定した電極表面にひびが入ったり、欠けたりすることのないため、性能が安定している。

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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NIPPON ZEON CO LTD

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(72)Inventor : MAEDA KOICHIRO

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### (54) BINDER FOR BATTERY, BINDER COMPOSITION, ELECTRODE AND BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a battery having stable performance by increasing an initial capacity, reducing a capacity decrease and decreasing chipping and crack ing in an electrode surface fixing an active material.

SOLUTION: A polyvinylidene fluoride system polymer (for instance, polyvinylidene fluoride) and a rubber polymer (for instance, polymer obtained as a latex particle by copolymerizing 40 pts.wt. styrene, 30 pts.wt. butadiene, 20 pts.wt. meacrylic acid methyl, 5 pts.wt. acrylonitrile, 5 pts.wt. itaconic acid) are fused or dispersed in a polarity organic solvent (for instance, N-methyl pyrrolidone), a battery binder composition is formed, active material (for instance, LiCo2 of positive electrode active material, carbon of negative electrode active material) is compounded therein, obtained slurry is applied to an electrode base unit, the solvent is removed, an electrode is formed, so as to manufacture a battery.

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### LEGAL STATUS

[Date of request for examination]

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EFFECT OF THE INVENTION

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[Effect of the invention] In the cell which used for any of a positive electrode and a negative electrode, or one side the electrode which fixed the active material using the binder constituent for cells of this invention, since [ which a capacity fall is small in order that an active material may seldom drop out of the electrode, initial capacity is large, and a crazing goes into the electrode front face which fixed the active material further, or is missing / things ] it is few, the performance is stable.

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**DETAILED DESCRIPTION**

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[Detailed description]

[0001]

[Field of the Invention] this invention relates to the binder constituent for cells with few degradations, the electrode using it, and a cell, even if the capacity of a cell is large and repeats charge and discharge still in detail about the binder constituent for cells, the electrode which used it, and a cell.

[0002]

[Prior art] The binder for cells is pasted up an electrode substrate front-face top, and an active material is fixed to an electrode front face by changing into the status that the active material was fixed in binder structure. The capacity of a cell falls as an active material will drop out of an electrode by not obtaining the cell with a big initial capacity, and repeating charge and discharge etc. if a binder cannot fix the active material of an amount to an electrode enough, although the capacity of a cell is decided according to two or more factors, such as a modality of active material, an amount, a modality of electrolytic solution, and an amount.

[0003] The binder for cells makes the binder constituent which usually melted or distributed the polymer used as a binder to the solvent distribute an active material, is applied to an electrode substrate front face, and fixes an active material to an electrode front face by volatilizing a solvent.

[0004] There are two kinds, an organic-solvent system binder constituent and a drainage-system binder constituent, as an organic-solvent system binder constituent, usually, what was melted in organic solvents, such as N-methyl pyrrolidone, is used, and poly-vinylidene full \*\*\*\*\* system polymers, such as poly-vinylidene full \*\*\*\*\*, are in a binder constituent (for example, a publication-number 249860 [ four to ] official report, a publication-number 201315 [ seven to ] official report, a publication-number 201316 [ seven to ] official report, etc.). The slurry which made this organic-solvent system binder constituent distribute an active material is applied to an electrode substrate, and although initial capacity of a cell can be enlarged if the electrode which removed and manufactured the organic solvent is used, when charge and discharge are repeated by the cell using this electrode, there is a problem that the active material fixed to the electrode tends to drop out. When it improved so that an active material may seldom drop out of an electrode substrate by introducing a polarity by carrying out copolymerization of the comonomer which has a polar group (for example, a publication-number 201315 [ seven to ] official report, a publication-number 201316 [ seven to ] official report, etc.), since the enhancement effect was small, and it swelled in the electrolytic solution and it became easy for an intensity to fall, with the binder which consists of a poly-vinylidene full \*\*\*\*\* system polymer, defluxion has not fully been suppressed.

[0005] What added the carboxyl methyl cellulose etc. as a thickener is used for the water variance liquid of the latex of the styrene butadiene rubber manufactured considering water as a solvent by the emulsion-polymerization method using the surfactant as a drainage-system binder constituent (for example, a publication-number 342966 [ four to ] official report, a publication-number 21068 [ five to ] official report, a publication-number 74461 [ five to ] official report, etc.). The slurry which made this drainage-system binder constituent distribute an active material was applied to the electrode substrate, and although the active material seldom dropped out of the electrode even if it repeated charge and discharge since an active material came to seldom drop out when the electrode which removed and manufactured moisture was used, the cell with a big capacity was not obtained.

[0006]

[Object of the Invention] Even if the purpose of this invention can enlarge capacity of a cell and it repeats charge and discharge, it is in offering the binder constituent for cells with few degradations, the electrode which fixed the active material using it, and a cell.

[0007]

[The means for solving a technical problem] Zealously, as a result of efforts, this invention persons find out that the constituent which blended the nature polymer of rubber with the poly-vinylidene full \*\*\*\*\* system polymer is hard to omit an active material as a binder, and came to complete this invention.

[0008] In this way, according to this invention, the cell using the electrode which fixed the active material with the binder for cells and this binder for cells which consist of a poly-vinylidene full \*\*\*\*\* system polymer and a nature polymer of rubber, and the binder and this binder for cells which consist of a solvent, and this electrode is offered.

[0009]

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[Gestalt of implementation of invention]

(The poly vinylidene full \*\*\*\*\* system polymer) 100 % of the weight is more preferably the most desirable in the repeat structural unit to which the poly-vinylidene full \*\*\*\*\* system polymer used by this invention originates in the vinylidene full ora id in a usual case 90% of the weight or more 80% of the weight or more preferably 50% of the weight or more. If there are too few repeat structural units originating in the vinylidene full ora id, it will become difficult for flexibility to run short, or for solvent resistance to be low, to fully fix an active material, and to make it maintain, without making it drop out. [0010] It is good also as a copolymer using the vinylidene full ora id and the comonomer which can be copolymerized in the domain which can be held, without fully fixing and omitting an active material if needed. An ethylenic unsaturated monomer is mentioned as such a comonomer. For example, styrene, an alpha methyl styrene, vinyltoluene, p-t-butyl styrene, Aromatic vinyl system monomers, such as \*\*\*\*\* styrene; (meta) Methyl acrylate, An ethyl acrylate, an acrylic-acid (meta) propyl, a butyl acrylate (meta), (Meta) (Meta) Acrylic-ester (meta) system monomers, such as isobutyl acrylate and acrylic-acid (meta) 2-ethylhexyl; (meta) Acrylamide, Acrylamide (meta) system monomers, such as N-methylol (meta) acrylamide and an N-butoxy methyl (meta) acrylamide; (meta) Metaglycidyl acrylate, Glycidyl group inclusion monomers, such as allyl glycidyl ether; (meta) Acrylonitrile (meta) system monomers, such as acrylonitrile; Acrylic acid, Carboxyl group inclusion monomers, such as a methacrylic acid, a crotonic acid, a fumaric acid, and an itaconic acid; Styrene sulfonic-acid \*\*\*\*\* sulfonic group inclusion monomers, such as an acrylamide methyl propane sulfonic acid; Amino-group inclusion monomers, such as methacrylic dimethyl aminoethyl and a methacrylic-acid diethylaminoethyl; etc. -- it is mentioned Although these most are monomers which have a polar group, in order that a binder may make it the thing excellent in the adhesive property, it is desirable to use the monomer which has a polar group as a comonomer in the case of making a poly-vinylidene full \*\*\*\*\* system polymer into a copolymer. In this case, copolymerization is carried out so that the repeat structural unit originating in a comonomer may become 10 or less % of the weight more preferably 20 or less % of the weight 50 or less % of the weight. If there are too many repeat structural units of the comonomer origin, a vinylidene full ora id origin repeat structural unit decreases too much, solvent resistance will be low and an active material will produce the problem become easy to drop out of an electrode substrate, by volume change by charge and discharge.

[0011] In an aqueous solvent or an organic solvent, using a persulfate, fault phosphate, etc. as a polymerization initiator, using the polymerization temperature of 40-140 degrees C, the polymerization pressure 1.4 - 14MPa, a polymerization initiator, an emulsifier, and a chain transfer agent, copolymerization of the poly-vinylidene full \*\*\*\*\* system polymer of this invention can be carried out, and it can be obtained. in addition, polymerization degree -- desirable -- 500 or more -- more -- desirable -- 800 or more -- and it takes or less for 2000 3000 or less preferably If polymerization degree is too small, intensities run short as a binder, if too large, viscosity will become high too much, and it becomes difficult to apply a binder constituent.

[0012] (Nature polymer of rubber) In this invention, in order to make a binder into what was more excellent in flexibility, the nature polymer of rubber is blended with a poly-vinylidene full \*\*\*\*\* system polymer, and it considers as a binder. Although especially the nature polymer of rubber is not limited, its nature polymer of rubber which has a polarity in that it excels in the adhesion with an active material and it excels in adhesion of an electrode substrate and an active material as a binder is desirable.

[0013] The nature polymer of polar rubber is a nature polymer of rubber which contains more preferably especially the repeat structural unit originating in the monomer (henceforth a polar monomer) which has a polarity 100 or less % of the weight 30% of the weight or more preferably 10% of the weight or more 5% of the weight or more. The problem that a polarity is small when there are few polar-monomer origin repeat structural units, and an active material tends to exfoliate from an electrode substrate may be produced, and it is hard coming to distribute to an organic solvent. As a polar monomer, ethylene nature nitril compound [, such as acrylonitrile (meta), croton nitril, and allyl-compound nitril, ]; etc. can be used.; Ethylene nature unsaturation carboxylates, such as methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, acrylic (meta) nitril, and hydroxyethyl (meta) acrylate; Ethylene nature unsaturated carboxylic acids, such as an acrylic acid, a methacrylic acid, an itaconic acid, a fumaric acid, and a maleic acid; Ethylene nature unsaturation carvone acid anhydrides, such as a Especially, dicarboxylic-acid anhydrides, such as dicarboxylic acids, such as an itaconic acid, a fumaric acid, and a maleic acid, and a maleic anhydride, etc. are desirable at the point which raises the bond strength of an electrode.

[0014] Moreover, since the balance of an intensity and flexibility is good, as for the nature polymer of polar rubber, it is desirable that they are an aromatic vinyl and a conjugated-diene system polymer. This desirable aromatic vinyl and conjugated-diene system polymer The repeat structural unit originating in the above-mentioned polar monomer preferably 5% of the weight or more 10 % of the weight or more, more -- desirable -- 30 % of the weight or more -- and 40 or less % of the weight more preferably 50 or less % of the weight Preferably especially 35 or less % of the weight, styrene, an alpha methyl styrene, vinyltoluene, The repeat structural unit originating in aromatic vinyl system monomers, such as p-t-butyl styrene, preferably 15 % of the weight or more, more -- desirable -- 20 % of the weight or more -- especially -- desirable -- 25 % of the weight or more -- and 50 or less % of the weight preferably Preferably especially 45 or less % of the weight 40 or less % of the weight, 1, 3-butadiene, The repeat structural unit originating in conjugated-diene system monomers, such as isoprene, 2, 3-dimethyl -1, 3-butadiene, 1, and 3-pentadiene, preferably 15 % of the weight or more, more -- desirable -- 20 % of the weight or more -- especially -- desirable -- 30 % of the weight or more -- and it is 40 or less % of the weight especially preferably 50 or less % of the weight more preferably 80 or less % of the weight When there are too many polar monomers, the property of an aromatic vinyl and a conjugated-diene system polymer seldom appears, and it is inferior to flexibility. If

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there is too little aromatic vinyl system monomer, or intensities run short if there is too much conjugated-diene system monomer, there is too much aromatic vinyl system monomer or there is too little conjugated-diene system monomer, flexibility runs short. If intensities run short, an active material will tend to drop out of an electrode substrate for volume change called swelling and deflation of the active material by charge and discharge, in case a cell will be assembled since an electrode is thin if flexibility runs short, also by slight deformation of an electrode, a binder becomes easy to exfoliate from an electrode substrate, and an active material tends to drop out of an electrode substrate.

[0015] Especially the manufacture technique of the nature polymer of rubber used for this invention is not limited, but although solution polymerization or an emulsion polymerization is sufficient, the polymerization also of the case of the aromatic vinyl and conjugated-diene system polymer which is a nature polymer of polar rubber is usually carried out by the emulsion polymerization as a latex particle from a simple thing etc. More than the dispersion-medium 60 weight section that generally makes water a principal component for the monomer mixture 100 weight section when carrying out an emulsion polymerization 200 weight section is distributed preferably more than 100 weight section and below 300 weight section. Preferably more than the emulsifier 1 weight section More than 2 weight section and below 10 weight section Preferably more than the polymerization initiator 0.1 weight section below 7 weight section More than 0.2 weight section and below 1 weight section -- desirable -- below 0.6 weight section -- further -- the molecular weight modifier of an initial complement -- in addition, the temperature of 30 degrees C or more -- desirable -- 50 degrees C or more -- and the polymerization of the 100 degrees C or less is carried out, stirring below 90 degrees C preferably After carrying out the polymerization of a part of batch method which carries out a polymerization after making a dispersion medium distribute all monomers beforehand, and monomer, you may carry out a polymerization by any of the semi batch method which adds and carries out the polymerization of the remaining monomer to a dispersion medium continuously, and the continuous method which adds and carries out the polymerization of the monomer to a dispersion medium continuously. As an emulsifier, polyoxyethylene alkyl ether, polyoxyethylene alkylphenol ether, Non-ionicity emulsifiers, such as a polyoxy ethylene oxide polypropylene-oxide copolymer; Alkyl sulfonate Alkyl allyl-compound sulfonate, alkyl sulfate, and alkyl sulfosuccinate

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EXAMPLE

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[Example] The example of reference, an example, and the example of a comparison are given to below, and this invention is concretely explained to it.

[0030] Styrene 400g, butadiene 300g, 200g [ of methyl methacrylates ], and acrylonitrile 50g, 50g of itaconic acids, 4g of lauryl ammonium sulfates, and 10g of sodium bicarbonates were added and stirred in 1l. of example of reference 1 water, and the monomer emulsion was prepared.

[0031] After heating at 80 degrees C, making it react for 1 hour and adding 80g of potassium persulfate with 200ml of water, adding and stirring 3.4l. of water, 10g of ethylenediaminetetraacetic acid, 10g of lauryl ammonium sulfates, 20g of potassium persulfate, and 10% of the weight of the above-mentioned monomer emulsion, the remaining monomer was continuously added at uniform velocity over 4 hours, and it was made to react to a pan for 4 hours. The remaining monomer was decompressed and removed and pH was adjusted to 7 by the lithium hydroxide. In addition, the invert ratio was about 99%.

[0032] 2000g N-methyl pyrrolidone was added to 250ml of the obtained latex variance liquid, moisture was removed using the evaporator, and latex-particle organic-solvent variance liquid was obtained. The mean particle diameter of the solid-content concentration of 9.3 % of the weight, the moisture of about 180 ppm, and a latex particle of this latex-particle organic-solvent variance liquid was 0.18 micrometers.

[0033] Latex-particle organic-solvent variance liquid was obtained like the example 1 instead of example of reference 2 styrene 400g, butadiene 300g, 200g [ of methyl methacrylates ], and acrylonitrile 50g, and 50g of itaconic acids except using styrene 500g, butadiene 250g, 150g [ of methyl methacrylates ], and acrylonitrile 100g. The mean particle diameter of the solid-content concentration of 7.0 % of the weight, the moisture of about 200 ppm, and a latex particle of this latex-particle organic-solvent variance liquid was 0.18 micrometers.

[0034] Latex-particle organic-solvent variance liquid was obtained like the example 1 instead of example of reference 3 styrene 400g, butadiene 300g, 200g [ of methyl methacrylates ], and acrylonitrile 50g, and 50g of itaconic acids except using styrene 350g, butadiene 200g, 200g [ of methyl methacrylates ], and acrylonitrile 100g, 100g of itaconic acids, and 50g of fumaric acids. The mean particle diameter of the solid-content concentration of 4.0 % of the weight, the moisture of 180 ppm, and a latex particle of this latex-particle organic-solvent variance liquid was 0.18 micrometers.

[0035] The binder constituent of this invention was obtained so that the amount of solid contents might become 3 weight section about the latex-particle organic-solvent variance liquid obtained among the example 1N-methyl pyrrolidone 30 weight section in the poly-vinylidene full \*\*\*\*\* (polymerization degree 1000 [ about ]) 5 weight section and the example 1 of reference.

[0036] the carbon (the product made from the Kansai thermology --) which is a negative-electrode active material to the amount of solid contents 8 weight section in a constituent at this binder constituent Add the NG-12L100 weight section, and N-methyl pyrrolidone is added so that viscosity may be set to about 7000cps. The slurry was prepared and it applied on copper foil with a thickness of 0.1mm, and at them, it held at 130 degrees C for 5 hours, and dried, the binder layer to which thickness fixed the active material uniform 0.5mm by the roll press was formed, and it considered as the electrode (negative electrode) of this invention.

[0037] Moreover, the same binder constituent is received at the amount of solid contents 4 weight section in a constituent. LiCo290 weight section which is a positive active material, and acetylene black (the DENKI KAGAKU KOGYO make --) a DIN -- a turnip -- the rack 10 weight section is added and viscosity is set to about 7000cps -- as -- N-methyl pyrrolidone -- in addition The slurry was prepared and it applied on aluminum foil with a thickness of 0.05mm, and at them, it held at 130 degrees C for 5 hours, and dried, the binder layer to which thickness fixed the active material uniform 0.5mm by the roll press was formed, and the electrode (positive electrode) was manufactured.

[0038] The two electrodes of a negative electrode and a positive electrode were clipped in a circle with a diameter of 15mm on the Teflon plate using the tubed blade. Neither the crack nor the chip accepted in the disconnection section of the active material layer fixed with the binder.

[0039] Made the separator which consists these two electrodes of a circular fine porosity layer (fiber nonwoven fabric) with a diameter [ of 16mm ], and a thickness of 50 micrometers made from polypropylene intervene, the active material layer each other fixed with the binder was made to counter, and it contained in the sheathing container made from the stainless steel which has arranged packing made from polypropylene (only for one, a base with the diameter of 20mm, a height [ of 1.8mm ], and a stainless steel thickness of 0.2mm is a certain cylindrical cup). Into a container, the electrolytic solution which melted

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LiPF<sub>6</sub> in concentration of one mol/l. at the solvent which mixed ethylene carbonate and diethyl carbonate to 1:1 by the volume ratio is poured in so that air may not remain. Put the cap of stainless steel with a thickness of 0.2mm, and fix a sheathing container and a cap through packing made from a pli propylene, and a contents is \*\*\*\*\* so that copper foil may contact a cap and aluminum foil may contact a container base, respectively. The coin type cell with a diameter [ of 20mm ] and a thickness of 2.0mm was manufactured.

[0040] 4.0V were charged with the galvanostatic process (current density: 1.0mA/cm<sup>2</sup>), on this cell, the charge and discharge which discharge to 3.0V were performed, and change of capacity was measured on it. The capacity in the 1st charge was 180mAh (100%), and was 160mAh (it falls to about 89%) in the 50th charge at 170mAh (it falls to about 94%), and the 100th charge.

[0041] Except using the latex-particle organic-solvent variance liquid obtained in the example 2 of reference instead of the latex-particle organic-solvent variance liquid obtained in the example 1 of example 2 reference, the electrode was produced like the example 1, the cell was obtained, and the performance was investigated.

[0042] Neither the crack nor the chip accepted in the disconnection section of the active material layer fixed with the binder with a diameter of 15mm of two electrodes clipped circularly. Moreover, the capacity in the 1st charge was 175mAh (100%), and was 155mAh (it falls to about 89%) in the 50th charge at 160mAh (it falls to about 91%), and the 100th charge.

[0043] Except using the latex-particle organic-solvent variance liquid obtained in the example 3 of reference instead of the latex-particle organic-solvent variance liquid obtained in the example 1 of example 3 reference, the electrode was produced like the example 1, the cell was obtained, and the performance was investigated.

[0044] Neither the crack nor the chip accepted in the disconnection section of the active material layer fixed with the binder with a diameter of 15mm of two electrodes clipped circularly. Moreover, the capacity in the 1st charge was 185mAh (100%), and was 160mAh (it falls to about 86%) in the 50th charge at 170mAh (it falls to about 92%), and the 100th charge.

[0045] Except using the binder constituent which added the poly-vinylidene full \*\*\*\*\* 10 weight section to the N-methyl pyrrolidone 90 weight section instead of the binder constituent prepared example of comparison 1, the electrode was produced like the example 1, the cell was obtained, and the performance was investigated.

[0046] The crack accepted in the disconnection section of the active material layer fixed with the binder with a diameter of 15mm of two electrodes clipped circularly, and the chip accepted in most fraction. Moreover, although the capacity in the 1st charge was 180mAh, since it fell to 20 or less mAh by the 40th time, measurement was stopped.

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**CLAIMS**

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[Claim]

[Claim 1] The binder for cells which consists of a poly-vinylidene full \*\*\*\*\* system polymer and a nature polymer of rubber.

[Claim 2] The binder for cells of the claim 1 publication whose nature polymer of rubber is a nature polymer of polar rubber.

[Claim 3] The claim 1 whose nature polymers of rubber are an aromatic vinyl and a conjugated-diene system copolymer, or the binder for cells given in two.

[Claim 4] The claims 1 and 2, or the binder for cells given in three and the binder which consists of a solvent.

[Claim 5] The electrode which fixed the active material with the claims 1 and 2 or the binder for cells given in three.

[Claim 6] The cell using the electrode of claim 5 publication.

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BATTERY BINDER, BINDER COMPOSITION, ELECTRODE, AND BATTERY  
[Denchiyou baindaa, baindaasoseibutsu, denkyoku, oyobi denchi]

Koichiro Maeda

UNITED STATES PATENT AND TRADEMARK OFFICE  
Washington, D.C. May 2003

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[Claims]

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[Claim 1] A battery binder consisting of a polyvinylidene fluoride polymer and a gum polymer.

[Claim 2] A battery binder of Claim 1 in which the gum polymer is a polar gum polymer.

[Claim 3] A battery binder of Claim 1 or 2 in which the gum polymer is an aromatic vinyl-conjugated diene copolymer.

[Claim 4] A binder consisting of the battery binder of Claim 1, 2, or 3 and a solvent.

[Claim 5] An electrode on which an active material is fixated by means of the battery binder of Claim 1, 2, or 3.

[Claim 6] A battery in which an electrode of Claim 5 is utilized.

[Detailed Explanation of the Invention]

[0001] [Field of Industrial Application]

The present invention pertains to battery binder compositions and to electrodes and batteries in which the compositions are utilized, more specifically to battery binder compositions that have large battery capacities and that suffer little deterioration after repeated charging and discharging and to electrodes and batteries in which the compositions are utilized.

[0002] [Prior Art]

A battery binder fixates an active material on an electrode surface by adhering to the electrode's base surface and by fixating the active material within the binder structure. The capacity of the battery is

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determined by multiple factors, such as the type and quantity of the active material, the type and quantity of the electrolyte, etc. A battery with a large initial capacity cannot be obtained unless the binder fixates a sufficient amount of active material to the electrode. In addition, the capacity of the battery decreases as the active material sheds from the electrode in repeated charging and discharging.

[0003] As for the battery binder, normally, an active material is dispersed in a binder composition obtained by dissolving and dispersing a polymer, which will be the binder, in a solvent. The mixture is applied on the electrode's base surface, the solvent is volatilized, and the active material thus becomes fixated to the electrode surface.

[0004] Binder compositions are divided into two types, which are organic solvent binder compositions and aqueous binder compositions. As an organic solvent binder composition, normally, a substance obtained by dissolving a polyvinylidene fluoride polymer, such as polyvinylidene fluoride, in an organic solvent, such as N-methylpyrrolidone, is utilized (for example, Kokai No.4-249860, Kokai No.7-201315, Kokai No.7-201316, etc.). The initial capacity of a battery can be increased by using an electrode produced by applying a slurry obtained by dispersing an active material in this organic solvent-type binder composition to the electrode base and by removing the organic solvent, but there is a problem in that the active material fixated to the electrode tends to shed when charging and discharging are repeated in a battery that contains the electrode. Even when an improvement is made by making it more difficult for the active material to shed from the electrode base by introducing polarity by

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copolymerizing a comonomer having polar groups (for example, Kokai No.7-201315, Kokai No.7-201316, etc.), the effect of the improvement is small when a binder is made of a polyvinylidene fluoride polymer, or the binder becomes swollen in the electrolyte and its strength becomes likely to decrease. Therefore, the shedding could not be inhibited sufficiently.

[0005] As an aqueous binder composition, a substance obtained by admixing carboxymethylcellulose as a thickener to a water-dispersed solution of a latex of styrene-butadiene copolymer rubber produced by using water as the solvent in an emulsion polymerization method using a surfactant is utilized (for example, Kokai No.4-342966, Kokai No.5-21068, Kokai No.5-74461, etc.). When an electrode made by applying a slurry, which is obtained by dispersing an active material in the aqueous binder composition, to the electrode base and by removing the water content is utilized, the active material becomes less likely to shed. Therefore, the active material becomes unlikely to shed from the electrode as a result of repeated charging and discharging, but a battery with a large capacity cannot be obtained.

[0006] [Problems that the Invention is to Solve]

The purpose of the present invention is to supply a battery binder composition that can increase the battery capacity and that suffers little deterioration in repeated charging and discharging and to supply an electrode and battery in which the active material is fixated by utilizing the battery binder composition.

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[0007] [Means for Solving the Problems]

As a result of diligent study, the present inventors discovered that a composition obtained by mixing a gum polymer with a polyvinylidene fluoride polymer works as a binder and makes it difficult for the active material to shed and thus completed the present invention.

[0008] In this manner, the present invention supplies a battery binder composed of a polyvinylidene fluoride polymer and a gum polymer, a binder consisting of said battery binder and a solvent, an electrode that has an active material fixated to it by means of said battery binder and solvent, and a battery in which said electrode is utilized.

[0009] [Working Mode of the Invention]

(Polyvinylidene fluoride polymer)

In the polyvinylidene fluoride polymer utilized in the present invention, it is preferred that the repeated structural units originating in vinylidene fluoride be 50 weight% or more, preferably 80 weight% or more, or more preferably 90 weight% or more, and in normal circumstances, 100 weight% is most preferred. If the repeated structural units that originate in vinylidene fluoride are too few, the flexibility becomes insufficient or the solvent resistance becomes too low, and it becomes difficult to fixate the active material adequately and to hold it by preventing it from shedding.

[0010] As necessary, it is permissible to obtain a copolymer by using a comonomer capable of copolymerizing with vinylidene fluoride as long as the active material can be adequately fixated and held without shedding. An ethylenic unsaturated monomer can be mentioned as such a comonomer,

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and the following can be mentioned as examples: aromatic vinyl monomers, such as styrene,  $\alpha$ -methylstyrene, vinyltoluene, p-t-butylstyrene, chlorostyrene, etc.; (meth)acrylic ester monomers, such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, etc.; (meth)acrylamide monomers, such as (meth)acrylamide, N-methyl (meth)acrylamide, N-butoxymethyl (meth)acrylamide, etc.; glycidyl-group-containing monomers, such as glycidyl (meth)acrylate, allyl glycidyl ether, etc.; (meth)acrylonitril monomers, such as (meth)acrylonitril; carboxyl-group-containing monomers, such as acrylic acid, methacrylic acid, crotonic acid, fumaric acid, itaconic acid, etc.; sulfonic-acid-group-containing monomers, such as sodium styrenesulfonate, acrylamide methylpropane sulfonic acid, etc.; amino-group-containing monomers, such as methacryl dimethyl aminoethyl, diethylaminoethyl methacrylate; etc. The majority of these are monomers containing polar groups. In order to make the adhesion of the binder excellent, it is preferred that a monomer containing polar groups be used as the comonomer that is utilized to turn the polyvinylidene fluoride polymer into a copolymer. In this case, copolymerization is performed in a manner such that the repeated structural units originating in the comonomer constitute 50 weight% or less, preferably 20 weight% or less, more preferably 10 weight% or less. If the repeated structural units originating in the comonomer are too numerous, the repeated structural units originating in vinylidene fluoride become insufficient, and problems occur in that the solvent resistance becomes low and the active material becomes likely

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to shed from the electrode base due to the volume change caused by charging and discharging.

[0011] The polyvinylidene fluoride polymer of the present invention can be obtained by allowing copolymerization to occur in an aqueous solvent or organic solvent by using persulfate, perphosphate, etc., as the polymerization initiator and by using an emulsifier, chain transfer agent, etc., at a polymerization temperature of 40~140°C and polymerization pressure of 1.4~14MPa. Moreover, the degree of polymerization should preferably be 500 or higher, more preferably 800 or higher, and preferably 3000 or lower, more preferably 2000 or lower. If the degree of polymerization is too low, the binder's strength becomes insufficient, and if the degree is too high, the viscosity becomes too high and it becomes difficult to apply the binder composition.

[0012] (Gum Polymer)

In the present invention, a gum polymer is combined with the polyvinylidene fluoride polymer to obtain a binder with better flexibility. Although the gum polymer is not particularly limited, a gum polymer having polarity is preferred since the binder will have superb adhesiveness to the active material and since excellent bonding can be achieved between the electrode base and the active material.

[0013] The polar gum polymer is a gum polymer containing preferably 5 weight% or more, more preferably 10 weight% or more, particularly preferably 30 weight% or more and 100 weight% or less of repeated structural units originating in a monomer with polarity (hereafter referred to as polar monomer). If the repeated structural units originating in the polar

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monomer are too few, problems such as the polarity being too weak and the active material peeling easily from the electrode base may occur. Also, the dispersion in an organic solvent becomes difficult to carry out. As the polar monomer, the following can be utilized: ethylenic nitrile compounds, such as (meth)acrylonitrile, crotonic nitrile, allylnitrile, etc.; ethylenic unsaturated carboxylic acid esters, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, (meth)acrylonitrile, hydroxyethyl (meth)acrylate, etc.; ethylenic unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, etc.; ethylenic unsaturated carboxylic anhydrides, such as maleic anhydride; etc. Dicarboxylic acids, such as itaconic acid, fumaric acid, maleic acid, etc., and dicarboxylic anhydrides, such as maleic anhydride, are preferred since they increase the bonding strength of the electrode.

[0014] Moreover, it is preferred that the polar gum polymer be an aromatic vinyl-conjugated diene polymer, since good balance between the strength and flexibility can be obtained. In this preferred aromatic vinyl-conjugated diene polymer, the repeated structural units originating in the above polar monomer are 5 weight% or higher, preferably 10 weight% or higher, more preferably 30 weight% or higher and preferably 50 weight% or less, more preferably 40 weight% or less, and even more preferably 35 weight% or less, the repeated structural units originating in an aromatic vinyl monomer, such as styrene,  $\alpha$ -methylstyrene, vinyltoluene, p-t-butylstyrene, etc., are preferably 15 weight% or higher, more preferably 20 weight% or higher, particularly preferably 25 weight% or

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higher and preferably 50 weight% or less, more preferably 45 weight% or less, and particularly preferably 40 weight% or less, and the repeated structural units originating in a conjugated diene monomer, such as 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, etc., are preferably 15 weight% or higher, more preferably 20 weight% or higher, particularly preferably 30 weight% or higher and preferably 80 weight% or less, more preferably 50 weight% or less, and particularly preferably 40 weight% or less. If the polar monomer is too much, it is difficult for the characteristics of the aromatic vinyl-conjugated diene polymer to be exhibited, and the flexibility will be poor. If the aromatic vinyl monomer is too little or the conjugated diene monomer is too much, the strength becomes insufficient. If the aromatic vinyl monomer is too much or the conjugated diene monomer is too little, the flexibility becomes insufficient. When the strength is insufficient, the volume change that occurs when the active material expands or shrinks as a result of charging or discharging makes the active material more likely to shed from the electrode base. If the flexibility is insufficient, the binder becomes likely to peel from the electrode base due to a slight deformation of the electrode that occurs when the battery is assembled since the electrode is thin, and the active material becomes likely to shed from the electrode base.

[0015] The manufacturing method for the gum polymer utilized in the present invention is not particularly limited. An aromatic vinyl- /4  
conjugated diene polymer that is a polar gum polymer may be obtained by either solution polymerization or emulsion polymerization, but for

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convenience, it is normally obtained as latex grains by means of emulsion polymerization. When performing emulsion polymerization, in general, 100 weight parts of a monomer mixture is dispersed in 60 weight parts or more, preferably 100 weight parts or more, and 300 weight parts or less, preferably 200 weight parts or less, of a dispersion medium. After adding 1 weight part or more, preferably 2 weight parts or more, and 10 weight parts or less, preferably 7 weight parts or less, of an emulsifier, 0.1 weight part or more, preferably 0.2 weight parts or more, and 1 weight part or less, preferably 0.6 weight parts or less, of an emulsion initiator, and a necessary amount of a molecular weight adjustor, polymerization is carried out by stirring at a temperature of 30°C or higher, preferably 50°C or higher, and 100°C or lower, preferably 90°C or lower. The polymerization may be carried out by one of a batch method in which polymerization is carried out after dispersing all of the monomer in a dispersion medium in advance, a semi-batch method in which part of the monomer is polymerized and in which the rest of the monomer is then continually admixed to the dispersion medium to be polymerized, or a continuous method in which polymerization is carried out by continually admixing the monomer to the dispersion medium. As the emulsifier, the following can be mentioned: nonionic emulsifiers, such as polyoxyethylene alkyl ether groups, polyoxyethylene alkyl phenol ether groups, polyoxyethylene oxide-polypropylene oxide copolymers, etc.; and anionic emulsifiers, such as alkyl sulfonate groups, alkyl sulfosuccinate groups, and polyoxyethylene alkylphenyl ether sarukueeto [as transliterated] groups. As the polymerization initiator, a persulfate, such as potassium

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persulfate, ammonium persulfate, etc., or a peroxide, such as hydrogen peroxide, benzoyl peroxide, cumene peroxide, tertiary butyl hydroperoxide, etc., is utilized. As necessary, a reducer, such as sodium bisulfite, ascorbic acid, etc., and/or a polymerization aid, such as disodium phosphate, may be admixed.

[0016] Moreover, in a case in which an aromatic vinyl-conjugated diene polymer that is a polar gum polymer is obtained by means of emulsion polymerization, the grain size of the polymer obtained as latex grains is  $0.01\mu\text{m}$  or larger, preferably  $0.05\mu\text{m}$  or larger, more preferably  $0.10\mu\text{m}$  or larger, and  $10\mu\text{m}$  or smaller, preferably  $1\mu$  or smaller, more preferably  $0.5\mu\text{m}$  or smaller. Moreover, in a case in which an aromatic vinyl-conjugated diene polymer that is a polar gum polymer is obtained by means of solution polymerization, the weight-average molecular weight in terms of polystyrene in gel permeation chromatography using tetrahydrofuran as the solvent should be 20,000 or more, preferably 30,000 or more, more preferably 50,000 or more, and 1,000,000 or less, preferably 800,000 or less, even more preferably 500,000 or less. If the grain size or molecular weight is too small, the adhesiveness becomes poor and the active material becomes likely to shed from the electrode substrate, and if they are too large, polymerization becomes difficult to perform.

[0017] (Battery Binder)

*new claims*  
For every 100 weight parts of the polyvinylidene fluoride polymer, the battery binder of the present invention contains 5 weight parts or more, preferably 20 weight parts or more, more preferably 40 weight parts or more, and 100 weight parts or less, preferably 90 weight parts or less,

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more preferably 80 weight parts or less, of the gum polymer. If there is too little gum polymer, the flexibility will be insufficient, which causes a slight strain in the electrode to peel the binder from the electrode substrate, and the active material layer on the electrode surface may crack or chip. On the contrary, if the amount is too much, the strength becomes insufficient, and the active material becomes likely to shed due to volume changes in the active material caused by charging and discharging.

[0018] (Battery Binder Composition)

The battery binder composition of the present invention is a battery binder solution or dispersed solution. Normally, for convenience, a binder composition is prepared by allowing optional ingredients, such as a polyvinylidene fluoride polymer, a gum polymer, etc., to dissolve or disperse in one solvent instead of preparing a binder in advance.

[0019] The solvent is not particularly limited as long as the polyvinylidene fluoride polymer and gum polymer can be dissolved or dispersed in it. In particular, if a polar gum polymer is used as the gum polymer, it is possible to disperse the gum polymer in a polar organic solvent, such as N-methylpyrrolidone, dimethyl fluoride, etc., in which the polyvinylidene fluoride polymer can be dissolved or dispersed readily. Moreover, even with a ketone type, such as acetone, methylethylketone, methylisobutylketone, etc., a furan type, such as tetrahydrofuran, rurufuraaru [as transliterated], etc., an ester type, such as ethyl acetate, methyl acetate, etc., or a nitrile type, such as acetonitrile, propionitrile, etc., in which polyvinylidene fluoride usually does not

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dissolve, polyvinylidene fluoride becomes dissolvable depending on the type and amount of the comonomer utilized for the polyvinylidene fluoride polymer, and solvents of these can also be utilized as long as a gum polymer can be dissolved or dispersed in them.

[0020] The amount of solvent is not particularly limited, either, but normally, preferably 400 weight parts or more, more preferably 500 weight parts or more, most preferably 800 weight parts or more, and preferably 10,000 weight parts or less, more preferably 5,000 weight parts or less, and most preferably 2,000 weight parts or less, of a solvent is used for every 100 weight parts of the binder. Either too much or too little of it makes it difficult to apply the binder composition.

[0021] (Electrode)

The electrode of the present invention can be obtained by preparing a slurry by combining an active material with the battery binder composition, applying it to the electrode base, and removing the solvent in order to solidify the active material in the matrix of the binder formed on the electrode base surface.

[0022] The active material utilized in the present invention is not particularly limited as long as it functions as an active material. Normally, carbon is utilized as the negative-electrode active material, and as the positive-electrode active material, a lithium-containing compound oxide, such as lithium manganese oxide, lithium cobalt oxide, lithium nickel oxide, lithium iron oxide, etc., can be utilized in addition to an oxide, sulfide, serinkabutsu [as transliterated], etc. of molybdenum, vanadium, titanium, niobium, etc. As the active material to

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be fixated, carbon is preferred since it becomes particularly firmly /5  
fixated inside the binder matrix and is unlikely to shed while being used  
as the battery's electrode.

[0023] The amount of the active material of the slurry utilized in  
the present invention is not particularly limited, either, but the active  
material is combined with the battery binder composition in a manner such  
that it is preferably 5 times or more, more preferably 7 times or more,  
and 1000 times or less, more preferably 100 times or less, than the battery  
binder in terms of weight. If the amount of the active material is too  
little, inactive areas increase on the surface of the binder layer to  
which the active material is fixated and its function as an electrode  
may become insufficient. If the amount of the active material is too much,  
the active material will not become sufficiently fixated to the electrode  
base and becomes likely to shed. In addition, the slurry is utilized after  
mixing a solvent with it in order to obtain a concentration that makes  
the application easy to carry out. *Mat.*

[0024] The electrode base utilized in the present invention is not  
particularly limited as long as it consists of a conductive material,  
but an article made of a metal, such as iron, copper, aluminum, etc.,  
is utilized in general. The shape is not particularly limited, either,  
but since a large electrode surface area is preferred, a sheet that is  
about 0.05~0.5mm in thickness is usually utilized.

[0025] The method for applying the slurry is not particularly limited.  
It is applied by means of immersion or brush coating, for example. The  
amount of coating should be adjusted so that the thickness of the binder

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layer to which the active material is fixated and that is obtained after removing the organic solvent will preferably be 0.1mm or more, more preferably 0.5mm or more, and preferably 5mm or less, more preferably 2mm or less. The method for removing the organic solvent is not particularly limited, either, but the organic solvent is normally removed by adjusting the degree of pressure reduction and the degree of heating so that the organic solvent will be volatilized as soon as possible within a speed range in which cracking does not occur in the binder layer due to stress concentration and in which shedding from the electrode base does not occur.

[0026] (Battery)

The battery of the present invention has the electrode of the present invention utilized for at least one of the positive electrode or negative electrode. This battery has a structure in which the sides of the positive electrode and negative electrode that have the active materials fixated to them (the binder-layer sides of the electrodes of the present invention) are made to face each other and in which an electrolyte is filled between the two electrodes. In the case of a large-scale battery, the electrodes are made to be tape-shaped, a separator sheet is sandwiched between and wrapped around the negative electrode and positive electrode, and these are immersed in a case filled with an electrolyte. In the case of a small-scale battery, the electrodes are made to be disk-shaped sheets and are immersed in an electrolyte filled in a coin-shaped case. By such methods, it is possible to obtain a battery that is easy to use and that has a large capacity.

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[0027] The electrolyte is not particularly limited, either. One that exhibits the functions of a battery should be selected in accordance with the types of the negative-electrode active material and the positive-electrode active material. For instance,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ ,  $\text{LiI}$ ,  $\text{LiAlCl}_4$ ,  $\text{LiPF}_6$ ,  $\text{NaClO}_4$ ,  $\text{NaBF}_4$ ,  $\text{NaI}$ ,  $(\text{n-Bu})_4\text{NClO}_4$ , etc. can be mentioned as examples of the electrolyte. As the solvent, the following can be mentioned as examples: ether types, ketone types, lactone types, nitrile types, amine types, amide types, sulfur compound types, chlorinated hydrocarbon types, ester types, carbonate types, nitro compound types, phosphoric ester compound types, sulfolane compound types, etc. In general, ethylene carbonate and diethyl carbonate are widely utilized.

[0028] (Modes)

As the modes of the present invention, the following can be mentioned as examples: (1) a battery binder consisting of a polyvinylidene fluoride polymer and a gum polymer; (2) a battery binder of (1) in which the gum polymer is a polar gum polymer; (3) a battery binder of (1) or (2) in which the gum polymer contains 5~100 weight% of repeated structural units originating in a monomer having polar groups; (4) a battery binder of one of (1)~(3) in which the gum polymer is an aromatic vinyl-conjugated diene copolymer; (5) a battery binder of one of (1)~(4) in which the gum polymer contains 5~50 weight% of repeated structural units originating in a monomer having polar groups, 15~50 weight% of repeated structural units originating in an aromatic vinyl monomer, and 15~80 weight% of repeated structural units originating in a conjugated diene monomer; (6) a battery binder of one of (1)~(5) in which the gum polymer is latex grains

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having a grain diameter of 0.01~10 $\mu$ m; (7) a battery binder of one of (1)~(5) in which the weight-average molecular weight of the gum polymer with respect to polystyrene in gel permeation chromatography in which tetrahydrofuran is used as the solvent is 20,000~1,000,000; (8) a battery binder of one of (1)~(7) in which the polyvinylidene fluoride polymer contains 50~100 weight% of repeated structural units originating in vinylidene fluoride; (9) a battery binder of one of (1)~(8) in which the degree of polymerization of the polyvinylidene fluoride polymer is 500~3,000; (10) a battery binder of one of (1)~(9) in which 5~100 weight parts of gum polymer is combined with 100 weight parts of polyvinylidene fluoride polymer; (11) a battery binder composition consisting of a solvent and one of (1)~(10); (12) a battery binder composition of (11) in which 400~10,000 weight parts of solvent is added to 100 weight parts of the battery binder; (13) an electrode in which an active material is fixated by means of the battery binder of one of (1)~(10); (14) an electrode of (13) in which 5~1000 times as much active material as the battery binder with respect to weight is fixated; (15) an electrode of one of (1)~(10) obtained by dispersing an active material evenly in the battery binder composition, by applying the mixture on the electrode base, and by removing the solvent; (16) a battery in which the electrode of one of (13)~(15) is utilized for at least one of the positive electrode or negative electrode; etc.

[0029] [Working Examples]

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In the following, the present invention will be explained concretely by mentioning reference examples, working examples, and comparative

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examples.

[0030] Reference Example 1

A monomer emulsion was prepared by admixing 400g of styrene, 300g of butadiene, 200g of methyl methacrylate, 50g of acrylonitrile, 50g of itaconic acid, 40g of ammonium lauryl sulfate, and 10g of sodium bicarbonate to 1 liter of water and by stirring the mixture.

[0031] 3.4 liters of water, 10g of ethylenediamine tetraacetic acid, 10g of ammonium lauryl sulfate, 20g of potassium persulfate, and 10g of the above monomer emulsion were mixed and were heated to 80°C while being stirred. After 1 hour of reaction, 80g of potassium persulfate was added together with 200ml of water. Then, the rest of the monomer was continually added at the constant speed over 4 hours, and 4 more hours of reaction was carried out. The residual monomer was removed by reducing the pressure, and the pH was adjusted to 7 by means of lithium hydroxide. The inversion rate was about 99%.

[0032] 2000g of N-methylpyrrolidone was added to 250ml of the obtained latex-dispersed solution, the water content was removed by using an evaporator, and a latex-grain organic solvent dispersed solution was obtained. This latex-grain organic solvent dispersed solution had a solid-content concentration of 9.3 weight%, about 180ppm of water content, and an average latex-grain diameter of 0.18 $\mu$ m.

[0033] Reference Example 2

A latex-grain organic solvent dispersed solution was obtained in the same manner as in Working Example 1 except for utilizing 500g of styrene, 250g of butadiene, 150g of methyl methacrylate, and 100g of acrylonitrile

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instead of 400g of styrene, 300g of butadiene, 200g of methyl methacrylate, 50g of acrylonitrile, and 50g of itaconic acid. This latex-grain organic solvent dispersed solution had a solid-content concentration of 7.0 weight%, about 200ppm of water content, and an average latex-grain diameter of 0.18 $\mu$ m.

[0034] Reference Example 3

A latex-grain organic solvent dispersed solution was obtained in the same manner as in Working Example 1 except for utilizing 350g of styrene, 200g of butadiene, 200g of methyl methacrylate, 100g of acrylonitrile, 100g of itaconic acid, and 50g of fumaric acid instead of 400g of styrene, 300g of butadiene, 200g of methyl methacrylate, 50g of acrylonitrile, and 50g of itaconic acid. This latex-grain organic solvent dispersed solution had a solid-content concentration of 4.0 weight%, 180ppm of water content, and an average latex-grain diameter of 0.18 $\mu$ m.

[0035] Working Example 1

The binder composition of the present invention was obtained by admixing 5 weight parts of polyvinylidene fluoride (degree of polymerization = about 1000) and 3 weight parts in terms of the solid content of the latex-grain organic solvent dispersed solution obtained in Reference Example 1 to 30 weight parts of N-methylpyrrolidone.

[0036] A slurry was prepared by adding to 8 weight parts of the solid content inside the binder composition 100 weight parts of carbon (NG-12L made by Kansai Netsugaku [as transliterated]), which is a negative-electrode active material, and N-methylpyrrolidone so that the viscosity became about 7000cps. The slurry was applied to a 0.1mm-thick

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copper foil and was dried by being kept at 130°C for 5 hours. A binder layer that had an even thickness of 0.5mm and in which the active material was fixated was made by means of a roll press and was made to be the electrode (negative electrode) of the present invention.

[0037] Moreover, a slurry was prepared by adding to the same binder composition 90 weight parts of  $\text{LiCo}_2$ , which is a positive-electrode active material, and 10 weight parts of acetylene black (Denkaburakku [as transliterated] made by Denki Kagaku Kogyo K.K.) for every 4 weight parts of the solid content of the binder composition and by adding N-methylpyrrolidone so that the viscosity became about 7000cps. The slurry was applied to 0.05mm-thick aluminum foil and was dried by being kept at 130°C for 5 hours. A binder layer that had an even thickness of 0.5mm and in which the active material was fixated was made by means of a roll press and was made to be the electrode (positive electrode).

[0038] Both negative and positive electrodes were cut out into 15mm-diameter circles on a Teflon plate by means of a cylindrical blade. No cracking or chipping was observed at the cut portions of the active-material layers fixated by the binders.

[0039] Both of these electrodes were placed in a stainless-steel external container (a cylindrical container that has only one bottom and that is 20mm in diameter, 1.8mm in height, and 0.2mm in stainless-steel thickness) provided with polypropylene packing by allowing the active material layers having the binders fixated to them to face each other with a separator that has a diameter of 16mm and a thickness of 50 $\mu\text{m}$  and that consists of a circular polypropylene microporous film (fiber nonwoven

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fabric) provided between them. An electrolyte was obtained by dissolving  $\text{LiPF}_6$  at a concentration of 1mol/litter in a solvent that is a 1:1 mixture of ethylene carbonate and diethyl carbonate in terms of volume and was injected into the container in a manner such that no air remained. A 0.2mm-thick stainless-steel cap was put on, the external container and the cap were fixated by means of the polypropylene packing, and the contents were sealed in a manner such that the copper foil touched the cap and the aluminum foil touched the container's bottom surface. Thus, a coin battery having a 20mm diameter and a 2.0mm thickness was prepared.

[0040] This battery was subjected to charging and discharging by means of a rated current method (current density = 1.0mA/cm<sup>2</sup>) in which the battery was charged to 4.0V and then discharged down to 3.0V, and the capacity changes were measured. The capacity at the first charging was 180mAh (100%), the capacity at the 50th charging was 170mAh (decreased to about 94%), and the capacity at the 100th charging was 160mAh (decreased to about 89%).

#### [0041] Working Example 2

Electrodes were prepared in the same manner as in Working Example 1 except for utilizing the latex-grain organic solvent dispersed solution obtained in Reference Example 2 instead of the latex-grain organic solvent dispersed solution obtained in Reference Example 1, a battery was obtained, and its performance was investigated.

[0042] No cracking or chipping was observed at the cut portions /7 of the active-material layers of both electrodes, which were cut out into circles of 15mm in diameter, fixated by the binders. The capacity at the

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first charging was 175mAh (100%), the capacity at the 50th charging was 160mAh (decreased to about 91%), and the capacity at the 100th charging was 155mAh (decreased to about 89%).

[0043] Working Example 3

Electrodes were prepared in the same manner as in Working Example 1 except for utilizing the latex-grain organic solvent dispersed solution obtained in Reference Example 3 instead of the latex-grain organic solvent dispersed solution obtained in Reference Example 1, a battery was obtained, and its performance was investigated.

[0044] No cracking or chipping was observed at the cut portions of the active-material layers of both electrodes, which were cut out into circles of 15mm in diameter, fixated by the binders. The capacity at the first charging was 185mAh (100%), the capacity at the 50th charging was 170mAh (decreased to about 92%), and the capacity at the 100th charging was 160mAh (decreased to about 86%).

[0045] Comparative Example 1

Electrodes were prepared in the same manner as in Working Example 1 except for utilizing a binder composition obtained by adding 10 weight parts of polyvinylidene fluoride to 90 weight parts of N-methylpyrrolidone instead of the prepared binder composition, a battery was obtained, and its performance was investigated.

[0046] Cracks were observed at the cut portions of the active-material layers of both electrodes, which were cut out into circles of 15mm in diameter, fixated by the binders. Chipping was also observed in a considerable number of areas. The capacity at the first charging was 180mAh,

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but the measurement was cancelled since it dropped to less than 20mAh at the 40th charging.

[0047] [Effects of the Invention]

In a battery in which an electrode having an active material fixated to it by means of a battery binder composition of the present invention is utilized for either one of the positive electrode or negative electrode, the active material is unlikely to shed from the electrode. Therefore, the capacity drop is small, the initial capacity is large, and there is only little cracking or chipping on the electrode surface to which the active material is fixated. Therefore, the performance is stable.

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